11

COVALENCY REDUCTION FACTORS IN THE CASE OF TETRAHEDRAL COMPLEXES

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ABSTRACT. Expressions for the reduction factors associated with the orbital contribution to magnetic moment and with the spin-orbit interaction in the tetrahedral complexes arising from the overlap of the central metal ion d-orbitals with the ligand s and p orbitals, have been deduced and discussed in the light of existing experimental results. It is seen that the ligand p-orbitals are more effective than s-orbitals.

INTRODUCTION

Superiority of the molecular orbital theory over the earlier introduced crystalline electric field theory (Van Vleck, 1932) in many of the compounds of the transition group of elements was first demonstrated by Van Vleck as early as 1935. In contrast to the crystalline field approximations where the basic orbitals are the pure central metal ion orbitals, in molecular orbital theory these are linear combinations of the central metal ion orbitals with the ligand orbitals allowed by symmetry of the complex. Hence the two orbitals have similar transformation properties and the matrix elements for the spin-orbit coupling H_{so} and the orbital angular momentum L, in the ligand field approximation can be represented by the old matrix elements multiplied by respective reduction factors arising from the admixtures. In the octahedral complexes, where the $d\epsilon$ orbitals belonging to the representation T_{2g} have the proper symmetry to form π-bonds with the ligands whereas $d\gamma$ orbitals belonging to the representation E_g can form σ-bonds with the ligands, the nature and order of the reduction factors have been investigated by Stevens (1953), Owen (1955), Tinkham (1956) and others.

In tetrahedral complexes such calculations are more cumbersome because $d\epsilon$ orbitals of the central ion have the proper symmetry to form both π and σ bonds with ligands. $d\gamma$ orbitals, however, can form only π-bonds. Our aim in this paper is to deduce expressions for these reduction factors and to discuss them in the light of existing experimental results on some tetrahedral complexes.

MOLECULAR ORBITALS OF COVALENT XY_4 TETRAHEDRAL COMPLEXES

The d-wave functions in a field of tetrahedral symmetry split up into two types $d\epsilon$ and $d\gamma$ spanning the representations T_2 and E respectively of the point group

T_d. In a molecular orbital schome the magnetic carriers remain partly in the central dc and $d\gamma$ orbitals and partly in surrounding ligand s and p orbitals. The form of the molecular orbital wavefunctions are as given by Wolfsberg and Helmoholz (1952)

$$|XY\rangle = N_t\left[d_{XY} + \frac{\lambda\sigma}{2}(\sigma_1+\sigma_4-\sigma_2-\sigma_3) + \frac{\lambda\pi t}{2}\left\{\frac{1}{2}(\pi_{x_1}+\pi_{x_2}-\pi_{x_3}-\pi_{x_4}) + \right.\right.$$

$$\left.\left. + \frac{\sqrt{3}}{2}(\pi_{y_1}+\pi_{y_2}-\pi_{y_3}-\pi_{y_4})\right\}\right]$$

$$|YZ\rangle = N_t\left[d_{YZ} + \frac{\lambda\sigma}{2}(\sigma_1+\sigma_3-\sigma_2-\sigma_4) + \frac{\lambda\pi t}{2}\left\{\frac{1}{2}(\pi_{z_1}+\pi_{z_2}-\pi_{z_3}-\pi_{z_4})\right.\right.$$

$$\left.\left. + \frac{\sqrt{3}}{2}(\pi_{y_1}+\pi_{y_2}-\pi_{y_3}-\pi_{y_4})\right\}\right]$$

$$|XZ\rangle = N_t\left[d_{XZ} + \frac{\lambda\sigma}{2}(\sigma_1+\sigma_2-\sigma_3-\sigma_4) + \frac{\lambda\pi t}{2}(\pi_{x_1}+\pi_{x_2}-\pi_{x_3}-\pi_{x_4})\right] \quad \ldots \quad (1)$$

$$|X^2-Y^2\rangle = N_e\left[d_{X^2-Y^2} + \frac{\lambda\pi e}{4}\{(\pi_{y_1}+\pi_{y_2}+\pi_{y_3}+\pi_{y_4})\right.$$

$$\left. + \sqrt{3}(\pi_{x_1}+\pi_{x_2}+\pi_{x_3}+\pi_{x_4})\}\right]$$

$$|3Z^2-r^2\rangle = N_e\left[d_{3Z^2-R^2} + \frac{\lambda\pi e}{}\{(\pi_{z_1}+\pi_{z_2}+\pi_{x_3}+\pi_{x_4})\right.$$

$$\left. + \sqrt{3}(\pi_{y_1}+\pi_{y_2}+\pi_{y_3}+\pi_{y_4})\}\right]$$

where N_t and N_e are the normalising constant and λ's are measure of amount of admixtures of the ligand s and p orbitals with the central d-orbitals

Choice of ligand coordinate axes are such that their z-axes always point towards the metal atom. All the σ-bonds are described by using z-coordinates and π-bonds by using x and y coordinates π_y orbitals are perpendicular to the plane formed by the central coordinate Y axis and the threefold symmetry axes of the point group T_d at the respective ligand The direction cosines of π_{y1} π_{y1} and $p\sigma_1$ with respect to the central coordinate system (Fig. 1) are respectively $\left(\frac{1}{\sqrt{6}} \quad -\sqrt{\frac{2}{3}} \quad \frac{1}{\sqrt{6}}\right)$ $\left(\frac{1}{\sqrt{2}} \quad 0 \quad \frac{1}{\sqrt{2}}\right)$ and $\left(-\frac{1}{\sqrt{3}} \quad -\frac{1}{\sqrt{3}} \quad -\frac{1}{\sqrt{3}}\right)$. Direction cosines of π's and σ's for other ligand sites can be obtained from these by making 180° rotations about the cubic axes (i.e. axes of the central coordinate system).

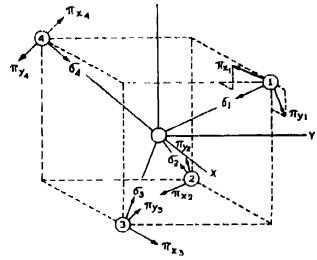

Fig. 1 Orientation of the Orbitals.

Further since both s and p orbitals can have σ-bonding with the metal atom, we can write

$$\lambda_\sigma |\sigma_i\rangle = \lambda_{\sigma p} |p_{\sigma i}\rangle + \lambda_{\sigma s} |s_i\rangle \qquad .. \quad (2)$$

where $$\lambda_{\sigma p}^2 + \lambda_{\sigma s}^2 = \lambda_\sigma^2$$

Wavefunctions t_2 and e in equation (1) can be expressed in a different form also, where x, y, z coordinate axes at the ligand sites are all parallel to X, Y, Z axes of the central coordinate system. This is

$$|XY\rangle = N_t|d_{XY} + A\{(|px1\rangle + |py1\rangle) + (|px2\rangle - |py2\rangle + (-|px3\rangle + |py3\rangle) + (-|px4\rangle - |py4\rangle)\} + B\{|pz1\rangle + |pz2\rangle + |pz3\rangle + |pz4\rangle\} + \frac{\lambda\sigma s}{2}\{|s_1\rangle + |s_4\rangle - |s_2\rangle - |s_3\rangle\}| \qquad .. \quad (3)$$

$$|YZ\rangle = N_t[d_{YZ} + A\{(|py1\rangle + |pz1\rangle) + (-|py2\rangle + |pz2\rangle) + (-|py3\rangle - |pz3\rangle) + (|py4\rangle - |pz4\rangle)\} + B\{|px1\rangle + |px2\rangle + |px3\rangle + |px4\rangle\} + \frac{\lambda\sigma s}{2}\{|s_1\rangle + |s_3\rangle - |s_2\rangle - |s_4\rangle\}]$$

$$|XZ\rangle = N_t[d_{XZ} + A\{(|px1\rangle + |pz1\rangle) + (-|px2\rangle - |pz2\rangle) + (-|px3\rangle + |pz3\rangle) + (|px4\rangle - |pz4\rangle)\} + B\{|py1\rangle + |py2\rangle + |py3\rangle + |py4\rangle\} + \frac{\lambda\sigma s}{2}\{|s_1\rangle + |s_2\rangle - |s_3\rangle - |s_4\rangle\}] \qquad ... \quad (3)$$

$$|X^2-Y^2>=N_e\Big[\, d_{X^2-Y^2} + \frac{\lambda\pi c}{2\sqrt{2}} \{(|px1\rangle - |py1\rangle)+(-|px2\rangle - |py2\rangle)$$

$$+(|px3>+|py3>)+(-|px4>+|py4>)\}\Big]$$

where

$$A = \frac{1}{2\sqrt{3}}\left(-\lambda_{\sigma p}+\frac{\lambda\pi t}{\sqrt{2}}\right)$$

$$B = \frac{1}{2\sqrt{3}}(-\lambda_{\sigma p}-\sqrt{2}\lambda\pi_t)$$

Here the notation of Stevens (1953) is followed in which, in each Ket vector the first letter denotes the type of orbit, the second angular dependence and the third the ligand to which it belongs

The new orbitals $|pxi>$, $|pyi>$ and $|pzi>$ can easily be related to the old ones π_{xi}, π_{yi}, p_{zi} with the help of usual transformation matrices utilising the direction cosines of π's and σ's.

CALCULATION OF REDUCTION FACTORS

(a) *Orbital reduction factors* :

There will be two orbital reduction factors occurring

(i) between a manifold of t_2 orbitals and

(ii) between a t_2 and e manifold.

We define them to be

$$\kappa = <t_2^+|L_z|t_2^+> : \kappa' = -\frac{1}{2i} < X^2-Y^2|L_z|XY >$$

where

$$t_2^+ = -\frac{i}{\sqrt{2}}[|XZ>+i|YZ>]$$

$$L_z = -i\hbar\Big[X\frac{\partial}{\partial Y} - Y\frac{\partial}{\partial X}\Big] \qquad \ldots (4)$$

L_z is expressed in the central coordinate system but while operating over ligand orbitals, has to be shifted to the ligand sites. Expressed in the new coordinate systems of the ligands (i.e. parallel to the central coordinate system), L_z is

$$\begin{aligned} L_z &= l_z^{(1)}+ap_y^{(1)}-ap_x^{(1)} && \text{at ligand site } 1\\ &= l_z^{(2)}-ap_y^{(2)}-ap_x^{(2)} && \text{" " " } 2\\ &= l_z^{(3)}+ap_y^{(3)}+ap_x^{(3)} && \text{" " " } 3\\ &= l_z^{(4)}-ap_y^{(4)}+ap_x^{(4)} && \text{" " " } 4 \end{aligned}$$

where $l_z^{(i)}$, $p_x^{(i)}\left(=-i\hbar\frac{\partial}{\partial x}\right)$, $p_y^{(i)}\left(=-i\hbar\frac{\partial}{\partial y}\right)$ are all expressed in the i-th

ligand new coordinate system and $2a$ is the edge of the cube in which the tetrahedron is inscribed (Fig. 1).

(i) Substituting for t_2^+ and operating with L_z we can deduce from eqns (4) and (3).

$$\kappa = \langle t_2^+ | L_z | t_2^+ \rangle$$

$$= N_t^2\left[1+4A^2-4B^2+16AS_2+8BS_1+4\lambda_{\sigma\sigma}S_3+4\sqrt{\frac{2}{3}}\,a\lambda_{\sigma\pi}S_4\right]$$

where $S_1 = \langle d_{xz}|py1\rangle = -\sqrt{\frac{2}{3}}\langle d_{xz}|\pi_{x1}\rangle - \frac{1}{\sqrt{3}}\langle d_{yz}|p_{\sigma 1}\rangle$

$$= -\sqrt{\frac{2}{3}}\,S_{t\pi} - \frac{1}{\sqrt{3}}\,S_{t\sigma p}\,.\; S_{t\pi} = \langle d_{xz}|\pi_{x1}\rangle \text{ and } S_{t\sigma p} = \langle d_{xz}|p\sigma_1\rangle$$

$$S_2 = \tfrac{1}{2}\{\langle d_{xy}|px1\rangle + \langle d_{xz}|pz1\rangle\} = \frac{1}{\sqrt{6}}\,S_{t\pi} - \frac{1}{\sqrt{3}}\,S_{t\sigma p} \qquad (5)$$

$$S_3 = \langle d_{xz}|s_1\rangle = S_{ts}$$

$$S_4 = \left\langle s_1\left|\frac{\partial}{\partial y}\right|py1\right\rangle = \left\langle s_1\left|\frac{\partial}{\partial x_1}\right|\pi_{x1}\right\rangle$$

and $$N_t^2 = [1+\lambda_\pi^2+\lambda_{\pi t}^2+4\lambda_{\sigma p}S_{t\sigma p}+4\lambda_{\pi t}S_{t\pi}+4\lambda_{\sigma s}S_{ts}]$$

In arriving at the result (5), it is found convenient to avoid the operation of the angular momentum operator L_z upon the ligand orbitals in the integrals of the form $\langle\psi_d|L_z|\psi_{ligand}\rangle$ by utilizing the Hermitian nature of the integrals (Stevens 1953). The only non-vanishing integrals involving a are those which involve the overlap integral S_4 also, the rest being monomials of order three and one, change sign with the inversion at the ligand sites and hence vanish. Further we have neglected the overlap between the two ligand orbitals at different sites.

Using eqn (5), κ can be expressed in the usual form as

$$= 1 - \tfrac{1}{2}\,\delta_1\lambda_\pi^2 N_t^2$$

where

$$\delta_1 = \left[2+\frac{3\lambda_{\pi t}^2}{\lambda_\pi^2}+\frac{2\sqrt{2}}{\lambda_\pi^2}\,\lambda_{\sigma p}\lambda_{\pi t}+\frac{8\sqrt{2}}{\sqrt{3}}\,\frac{a\lambda_{\sigma\pi}S_4}{\lambda_\pi^2}\right]$$

(ii) For κ', we proceed in a similar way and obtain

$$\kappa' = \frac{1}{2i}\langle X^2-Y^2|L_z|XY\rangle$$

$$= N_t N\,[1+\sqrt{2}A\lambda_{\pi\sigma}+\sqrt{2}\lambda_{\pi\sigma}(S_{1x}{}^1+S_{1y}{}^1)+8AS_2+\sqrt{2}\lambda_{\sigma p}S_1$$

$$+\sqrt{2}a\lambda_{\pi\sigma}\lambda_{\sigma\pi}S_4] \qquad \ldots (7)$$

In the above equation, we define

$$S_{1x^1}+S_{1y^1} = \langle d_{x^2-y^2}|px\rangle - \langle d_{x^2-y^2}|py\rangle = \frac{1}{\sqrt{3}}\left(\sqrt{3}\langle d_{x^2-y^2}|\pi x_1\rangle + \langle d_{x^2-y^2}|\pi y_1\rangle\right) \sqrt{2}S_{e\pi} \quad \ldots (8)$$

where $$S_{e\pi} = \left\langle d_{x^2-y^2}\left|\frac{\sqrt{3}\pi_{x_1}+\pi_{y_1}}{2}\right.\right\rangle$$

and S_2, S_3 and S_4 are same as in eqn. (5) and the normalising constant N_e^2 is given by

$$N_e^2 = [1+4\lambda_{\pi e}S_{e\pi}+\lambda_{\pi e}^2]$$

and

$$N_tN_e \simeq [1+2\lambda_{\pi e}S_{e\pi} - \frac{2\sqrt{2}}{3}\lambda_{ap}S_{t\pi} + \frac{4}{3}\lambda_{ap}S_{top}$$

$$+ \frac{2}{3}\lambda_{\pi t}S_{t\pi} + \frac{2\sqrt{2}}{3}\lambda_{\pi t}S_{top} + 2\lambda_{p\pi}S_{tne} \quad \ldots (9)$$

$$\frac{1}{3}\lambda_{\pi e}^2 + \frac{1}{3}(\lambda_{ap}^2+\lambda_{\pi t}^2)+\frac{1}{3}\lambda_{ae}$$

Using (9) and (7), κ' is again expressed in the form

$$\kappa' = 1 - \frac{1}{2}\lambda_a^2\delta_2(N_tN_e) \quad . \quad (10)$$

where

$$\delta_2 = \left[1 + 2\sqrt{2}(\sqrt{2}-1)\frac{\lambda_{ae}}{\lambda_a^2}S_{tae} + \frac{\lambda_{\pi t}^2+\lambda_{\pi e}^2}{\lambda_a^2}\right.$$

$$\left.\sqrt{\frac{2}{3}}\frac{\lambda_{ap}\lambda_{\pi e}}{\lambda_a^2} - \frac{1}{\sqrt{3}}\frac{\lambda_{\pi t}\lambda_{\pi e}}{\lambda_a^2} + 2\sqrt{2}\frac{\lambda_{\pi e}\lambda_{ae}}{\lambda_a^2}S_4\right]$$

(b) *Reduction factors for Spin-Orbit coupling*

Here again since we are concerned mainly with the ligand atoms with smaller atomic numbers we confine to the approximation made by Owen (1955), originally for octahedral complexes, that the spin-orbit coupling is only effective at the central metal ion and so the reduction factors with $\langle t_2^+|$ $|t_2^1\rangle$ and $\langle t_2^+|$ $|e\rangle$ manifold are, respectively

$$\begin{aligned} R_t &= N_t^2 \\ R' &= N_tN_e \end{aligned} \quad (11)$$

DISCUSSION

The expressions for reduction factors are quite complicated and involve a number of unknown parameters. However some qualitative results can be easily inferred if we stick to some approximations. Thus in above expressions terms involving a are small (since a itself is very small $\sim 10^{-8}$ cm) and can be neglected. Furthermore the study in molecular bonding in the case of octahedral complexes has shown that usually σ-bonding is more important than π-bonding, in the case of tetrahedral complexes this is not very obvious. However lacking detailed information if for the present, this approximation is made (i.e. if we put $\lambda_{\pi t} \simeq \lambda_{\pi e} \simeq 0$). Our expressions for κ and κ' reduce to

$$\kappa = 1 - \tfrac{1}{2}\,\delta_1 \lambda_{\sigma}^2 N_t^2 \qquad \ldots (12)$$

where $\delta_1 = 2$

$$N_t^2 = [1 + \lambda_{\sigma}^2 + 4\lambda_{\sigma p} S_{t\sigma p} + 4\lambda_{\sigma s} S_{t\sigma s}]^{-1}$$

and $$\kappa' = 1 - \tfrac{1}{2}\,\delta_2 \lambda_{\sigma}^2 (N_t N_e)$$

where $$\delta_2 = \left[1 + 2\sqrt{2}(\sqrt{2}-1)\,\frac{\lambda_{\sigma s}}{\lambda_{\sigma}^2}\,S_{t\sigma s}\right] \qquad \ldots (13)$$

$$N_t N_e = \left[1 - \frac{2\sqrt{2}}{3}\,\lambda_{\sigma p} S_{t\pi} + \frac{4}{3}\,\lambda_{\sigma p} S_{t\sigma p} + 2\lambda_{\sigma s} S_{t\sigma s} + \tfrac{1}{2}\,\lambda_{\sigma p}^2 + \tfrac{1}{2}\,\lambda_{\sigma s}^2\right]^{-1}$$

In the tetrahedral complexes of our concern quite often the ligands are either oxygen or chlorine type with $2s$, $2p$ or $3s$, $3p$ electrons respectively taking part in bonding. AM O. calculation of the energy spectrum in the case of MnO_4^{--} and CrO_4^{--} complexes has been done by Wolfsberg and Helmholz (1952). They have made a further simplifying assumption that only $2p$ electrons of oxygen take part in bonding and electrons filling upto $2s$ orbits form a closed shell. Under this assumption (i.e. $\lambda_{\sigma s} = 0$, $\lambda_{\sigma p} = \lambda_{\sigma}$) the equations are further simplified to

$$\delta_1 = 2 \qquad \ldots (14)$$

$$N_t^2 = [1 + \lambda_{\sigma}^2 + 4\lambda_{\sigma p} S_{t\sigma p}]^{-1}$$

$$\delta_2 = 1$$

$$N_t N_e = \left[1 - \frac{2\sqrt{2}}{3}\,\lambda_{\sigma p} S_{t\pi} + \frac{4}{3}\,\lambda_{\sigma p} S_{t\sigma p} + \frac{1}{2}\,\lambda_{\sigma p}^2\right]^{-1} \qquad \ldots (15)$$

Using the parameters mainly obtained from intensity consideration (Wolfsberg, Helmholz, 1952; Ballhausen and Liehr, 1958, Viste and Gray, 1964)

$$S_{t\pi} = \frac{3 \times .151}{2\sqrt{2} \times 4} \; ; \; S_{t\sigma p} = -\frac{\sqrt{3} \times .167}{2 \times 4} \; ; \; \lambda_{\sigma s} \simeq \lambda_{\sigma p} \simeq \frac{1}{\sqrt{2}}$$

(Table 1) for MnO_4^{--}, we have $\kappa = .533$, $\kappa' = .678$ and $R = .476$, $R' = .641$.

TABLE I

Salt	κ	κ′	R	R′	Values of parameters	References
MnO^{-}_{4}	.533	.678	.476	.641 (for $\lambda_{\sigma s}=0$)	$S_{t\pi} = \frac{3\times 151}{2\sqrt{2}\times 4}$ $S_{t\sigma p} = -\frac{\sqrt{3}\times 167}{2\times 4}$	Wolfsberg and Helmholz, 1952 Ballhausen and Liehr, 1958.
	.502	.678	.512	.676 (for $\lambda_{\sigma s}=\lambda_{\sigma p}$)	$S_{t\sigma s} = \frac{246\times\sqrt{3}}{2\times 4}$ $\lambda_{\pi} = -\sqrt{(1-\alpha^2)}/\alpha \cdot \alpha = -\frac{1}{\sqrt{2}}$ $\lambda_{\sigma s} = \lambda_{\sigma p} = -\frac{1}{\sqrt{2}}$	Viste and Gray, 1964.
$CrO^{=}_{4}$	.551	.683	.691	633	$S_{t\sigma p} = (11\times\sqrt{3})/(2\times 4)$ $S_{t\pi} = (18\times\sqrt{3})/2\sqrt{2}\times 4$ $\lambda_{\sigma} = \lambda_{\sigma p} = -1$ $\alpha = 1/\sqrt{2}$	Wolfsberg and Helmholtz, 1952 Ballhausen and Liehr, 1958
Co++ in KCl	.799	.891	.775	.877	$S_{t\sigma p} = -8\ 59\times 10^{-2}/4$ $S_{t\pi} = 2\ 25\times 10^{-2}/4$ $\lambda_{\sigma\tau} = -0\ 5$	Washimiya, 1963
$CoCs_3Cl_5$	.419	.563	380	.584	$S_{t\sigma p} = -\ 0947/4$ $S_{t\pi}$ = same as Co++ in KCl $\lambda_{\pi} = \lambda_{\sigma p} = \frac{\sqrt{1-\alpha^2}}{\alpha}$ $= -1\ 224$ $\therefore\ \alpha = \sqrt{\frac{4}{10}}$	Ballhausen and Liehr, 1958 Washimiya, 1963.

Ballhausen and Liehr (1958), however pointed out a serious mistake in the assignment of bands made by Wolfsberg and Helmholz (1952) for MnO^-_4 and they further undertook above investigation considering also the 2*s* orbitals as taking part in bonding (i.e. $\lambda_{as} \neq 0$) If we utilize this parameter, we have for MnO^-_4

$$\kappa = .502,\ \kappa' = .678,\ R = .512 \text{ and } R' = .676 \text{ (Table I)}$$

Thus we see that whatever be the effect on band energy calculation of the approximation that 2*s* and 3*s* orbitals do not take part in bonding, for the calculation of reduction factors it is a fairly good approximation

Results of calculations for several tetrahedral complexes are summed up in Table I

Our reduction parameters for $CoCs_3Cl_5$ derived semiempirically from susceptibility measurement are $\kappa' = .92$ and $R' = .83$ which are appreciably different from the present values $\kappa' = .653$ and $R' = 584$ (Table I). The descrepancy may be due to the fact that in tetrahedral complexes π-bonding also play an equally important role as σ-bonding. This is actually so is definitely proved for the cases of MnO_4^{--} and CrO_4^{--} by Wolfsberg and Helmholz (1952). For the present, however, we cannot go to further details due to the insufficient knowledge about the parameters needed.

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